



AFRL-AFOSR-JP-TR-2016-0075

Metal Nanoshells for Plasmonically Enhanced Solar to Fuel Photocatalytic Conversion

Randall Lee
UNIVERSITY OF HOUSTON SYSTEM

05/18/2016
Final Report

DISTRIBUTION A: Distribution approved for public release.

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/ IOA
Arlington, Virginia 22203
Air Force Materiel Command

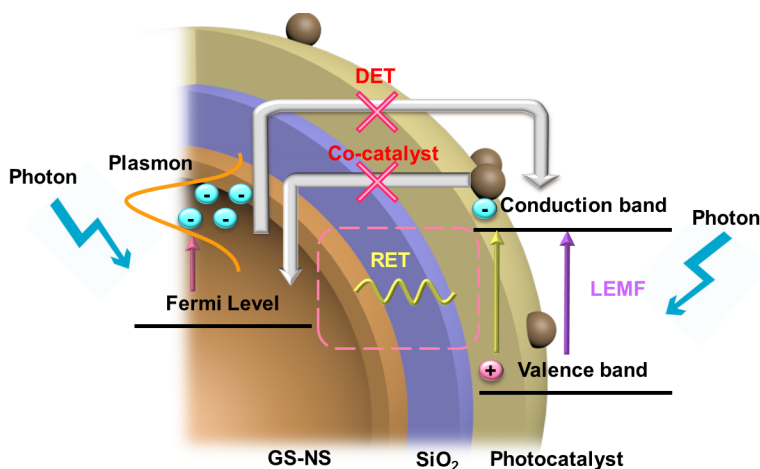
REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
<p>The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services, Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.</p> <p>PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.</p>					
1. REPORT DATE (DD-MM-YYYY) 19-05-2016		2. REPORT TYPE Final		3. DATES COVERED (From - To) 25 Jun 2014 to 24 Dec 2015	
4. TITLE AND SUBTITLE Metal Nanoshells for Plasmonically Enhanced Solar to Fuel Photocatalytic Conversion				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER FA2386-14-1-4074	
				5c. PROGRAM ELEMENT NUMBER 61102F	
6. AUTHOR(S) Randall Lee				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) UNIVERSITY OF HOUSTON SYSTEM 4800 CALHOUN ST STE 316 HOUSTON, TX 77204-0001 US				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) AOARD UNIT 45002 APO AP 96338-5002				10. SPONSOR/MONITOR'S ACRONYM(S) AFRL/AFOSR IOA	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) AFRL-AFOSR-JP-TR-2016-0075	
12. DISTRIBUTION/AVAILABILITY STATEMENT A DISTRIBUTION UNLIMITED: PB Public Release					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT <p>First thrust: Gold-silver nanoshells (GS-NSs) that provide a tunable localized surface plasmon resonance (LSPR) were prepared for incorporation into a photocatalytic matrix to facilitate charge separation of photo-excited carriers. Zinc indium sulfide (ZIS), a visible light-active photocatalyst, was used as the photocatalytic matrix. In addition, a dielectric interlayer of silica between the GS-NSs and ZIS was used to provide an additional parameter to distinguish the enhancement mechanism. In an extensive study using ten different samples, we found that GS-NS@ZIS particles with an LSPR absorption at ~700 nm and a silica interlayer of ~17 nm generated a rate of hydrogen production 2.6 times higher than that of unmodified ZIS. Second thrust: Tin oxide-coated gold-silver nanoshells were prepared as an alternative plasmonic enhancement system to the silicon oxide system described above. Tin oxide is an attractive material for photocatalytic reactions due to its exceptional photostability and good carrier mobility; however, instead of blocking direct electron transfer, we anticipate this interlayer will modulate charge transfer from the metal to the semiconductor and vice versa. These new core-shell particles were sent to our collaborator, Prof. Tai-Chou Lee at NCU in Taiwan, for evaluation.</p>					
15. SUBJECT TERMS hydrogen generation, metal nanoshells, photocatalyst					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT SAR	18. NUMBER OF PAGES 4	19a. NAME OF RESPONSIBLE PERSON CASTER, KENNETH
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 315-229-3326

Final Report – AFOSR Grant FA2386-14-1-4074

In the set of experiments pursued under this grant, gold-silver nanoshells (GS-NSs) that provide a tunable localized surface plasmon resonance (LSPR) were used to boost the yield of photocatalytically generated hydrogen from water. A manuscript detailing the work on this project was initially submitted to *ACS Applied Materials & Interfaces* in mid 2015, but the reviewers requested extensive additional experimental work, which delayed peer-reviewed publication until this spring.¹ For this study, composite nanostructures were prepared starting with the GS-NS cores, which were then coated with a thin layer of silica (SiO_2), followed by a zinc indium sulfide (ZnIn_2S_4 ; ZIS) semiconductor shell. The blended-metal GS-NS cores were employed to facilitate charge separation of photo-excited carriers within the surrounding ZIS matrix. The LSPR property of the nanoshells (i.e., the ability of the metals to absorb photons that are in resonance with the frequency of the conduction band electrons of the metal) leads to a redistribution of the absorbed energy via various dissipative mechanisms. This energy transfer can enhance the photoactivity of the system because ZIS is a visible light-active photocatalyst, which for our experiments was synthesized as a ZIS matrix with a band gap of ~ 2.25 eV, producing an extrapolated absorption edge in its UV-visible spectrum of ~ 550 nm.

The three types of GS-NS cores that we prepared and tested exhibited intense extinctions at ~ 500 , 700, and 900 nm, providing a boost in energy to the system. The thicknesses of three different SiO_2 interlayers (~ 17 nm, ~ 42 nm, or no SiO_2) between the GS-NSs and the ZIS photocatalyst provided a means of comparing dielectric barrier properties that helped determine the energy-transfer mechanism(s) that were active for this system. In particular, the direct transfer of hot electrons from the LSPR-activated GS-NSs to the ZIS photocatalyst was blocked by the silica interlayer. Overall, ten samples were prepared, with the highest H_2 gas evolution rate observed for GS-NS particles having an SPR extinction peak at ~ 700 nm and a SiO_2 interlayer thickness of ~ 17 nm; importantly, the rate of H_2 production was 2.6 times higher than that of ZIS with no GS-NSs. These studies (1) demonstrate the existence of coupling between the SPR of the GS-NSs and the absorption of light by ZIS and (2) show that the presence and thickness of the silica interlayer provides key parameters for optimizing solar-based hydrogen production. Therefore, the recent publication of these results provides useful information for the design of plasmon-enhanced photocatalysts for generating H_2 from water.¹

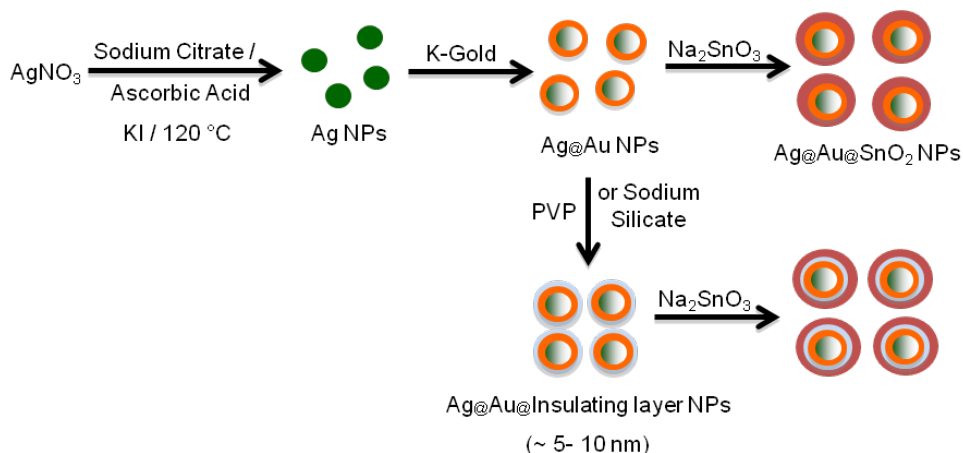
Scheme 1. Illustration of Energy Transfer Mechanisms for SiO_2 -Coated GS-NSs in a ZIS Matrix



In the second set of experiments pursued under this grant, we developed two synthetic approaches for preparing tin oxide-coated gold-silver nanoshells, as illustrated in Scheme 2. These particles were synthesized to compare the performance of these unique nanoshells to that of the first-generation silica-coated GS-NSs in our ZIS photocatalytic system. Tin oxide is a promising coating material for photocatalytic reactions due to its exceptional photostability and good carrier mobility; however, the latter feature means that the coating will play a slightly different role in our composite particle system. Instead of blocking direct electron transfer, we anticipate that thin shells derived from tin oxide and doped tin oxides will modulate charge transfer from the metal to the semiconductor and vice versa. We believe that this alternative shell architecture can further enhance the efficiency of the photocatalytic reactions occurring in the surrounding photocatalyst matrix. Studies of this system will also allow us to develop a better understanding of the fundamental mechanisms occurring within this composite particle system via direct comparisons to the composite particles containing silica-coated GS-NSs.

Additionally, we previously reported that tin oxide-coated gold nanoparticles are markedly more stable than silica-coated gold nanoparticles over a wide range of pH values (*ACS Appl. Mater. Interfaces* **2013**, 5, 2479). Such an improvement in stability not only offers alternative routes to the synthesis of our composite photocatalytic particles, but also offers functional particle architectures under extreme conditions (e.g., high pH). Samples of this new type of core-shell particle have been shipped to our collaborator, Professor Tai-Chou Lee, at National Central University in Taiwan, along with other particles of equivalent light absorptions that are either silica-coated or non-coated, for further testing using the ZIS photocatalyst.² Synthetic procedures for preparing doped versions of these tin oxide-coated nanoshells using antimony, indium, and zinc as dopants are also being pursued, but are still under development.

Scheme 2. Strategy for the Synthesis of Tin Oxide-Coated Gold-Silver Nanoshells



Publication List:

1. Li, C.-H.; Li, M.-C.; Liu, S.-P.; Jamison, A. C.; Lee, D.; Lee, T. R.; Lee, T.-C. Plasmonically Enhanced Photocatalytic Hydrogen Production from Water: The Critical Role of Tunable Surface Plasmon Resonance from Gold-Silver Nanoshells. *ACS Appl. Mater. Interfaces* **2016**, just accepted manuscript. DOI: 10.1021/acsami.6b01197
2. Li, C.-H.; Kolhatkar, A.; Jamison, A. C.; Lee, T.-C.; Lee, T. R. Tunable Plasmonic Core@Shell Nanostructures, manuscript in preparation.